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INVESTIGATE MATERIAL SYSTEMS FOR  
MIRRORS USED IN HIGH POWER CO AND CO<sub>2</sub>  
LASERS

R. W. Stewart

Battelle-Pacific Northwest Laboratories

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IN HIGH POWER CO AND CO<sub>2</sub> LASERS

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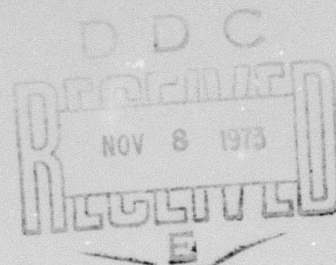
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SEMIANNUAL TECHNICAL REPORT

ABSTRACT

An IR metal mirror with up to ~99.2% reflectivity and a surface roughness of about 15 Å rms was developed using high-rate sputter-deposition techniques. The necessary smooth, high-conductivity surface was obtained by applying two sequentially deposited metal layers on a high-conductivity metal mirror support (OFHC). The principal property of the first deposit was its polishability and of the second its high electrical conductivity. The required smooth surface was obtained by depositing and mechanically polishing a dispersion-hardened (1 vol.%SiC in Cu), stable, fine-grained material about 0.5 mm thick.

A high-conductivity surface was achieved by depositing high-purity copper or silver layers which were about 0.15 μm thick. Optimum sputtering conditions for production of thin, high-conductivity overlayers were determined to include high substrate temperature, low deposition rate, and minimal sputter etching of the substrate before deposition.

Preliminary measurements of damage thresholds indicate that this mirror material system is superior to conventionally prepared metal mirrors.

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INTRODUCTION

The purpose of this report is to describe the progress made during Phase II of the investigation of material systems for high-reflectivity infrared (IR) mirrors used in high power CO and CO<sub>2</sub> lasers. It is the second phase of an 18-month, 3-phase program being conducted by Battelle Northwest Laboratories (BNW) in close cooperation with the Naval Weapons Center (NWC) at China Lake, California.

Front surface, high-reflectivity laser mirrors have received increased attention in the last few years. Power densities of several kW/cm<sup>2</sup> are anticipated on cavity optics components, both for continuous wave (CW) and pulsed IR laser applications. It is generally conceded that mirrors for such applications require reflectivities of  $\geq 99.9\%$ .<sup>(1)</sup> In addition, to obtain the thermal conductivity required for heat dissipation, metal mirror components are considered essential wherever their use is feasible.

The mirror structure visualized initially consists of the following components listed in their sequence of formation:

- 1) A metal mirror support on which will be deposited successive layers of material by sputtering or ultrahigh vacuum evaporation. The mirror support material selected for the initial work will be OFHC (Oxygen Free High Conductivity) copper.

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(1) C. M. Stickley, "Conference on High-Power Infrared Laser Window Materials," (C. S. Sahagian and C. A. Pitha, eds.) Air Force Cambridge Research Labs Special Report No. 127, p. 405, November 1971.



- 2) A hard, stable, fine-grained, sputter-deposited metal mirror material whose principal property will be its ability to be polished to a surface roughness  $\leq 20 \text{ \AA rms}$ .
- 3) A thin, high-conductivity, sputter-deposited or evaporated metal overlayer having a high-reflectivity surface.
- 4) A minimum-components, dielectric, quarter-wavelength reflectivity enhancement coating to improve the reflectivity of the surface achieved in 3) above. The minimum-layer limitation is derived from the low conductivity of the dielectric material and the realization that the expected several  $\text{watts/cm}^2$  of absorbed power may cause spallation of the dielectric.

The investigation conducted during Phase I was concentrated on the two first elements of the proposed structure; the work in Phase II has been concentrated on the third element--the high-conductivity, sputter-deposited overlayer. The results obtained during Phase I are published in the Semi-annual Technical Report, "Investigate Material Systems for Mirrors Used in High Power CO and CO<sub>2</sub> Lasers," BNWL-1780, December 1972; this report will hereafter be referred to as the Phase I report.

The main goals set forth for the initial phase were all satisfactorily achieved. Copper, dispersion hardened with additions of 0.5 to 5 vol% SiC or Al<sub>2</sub>O<sub>3</sub>, was deposited by high-rate sputtering to produce stable, fine-grained ( $< 0.4 \text{ \mu m}$ ) polishable material which exhibited a surface roughness of less than  $15 \text{ \AA rms}$  when it was mechanically polished. The polishing techniques were developed for achieving these smooth surfaces.

Instruments were also designed, constructed and operated successfully for measuring surface roughness by scattered light and mirror absorption by differential calorimetry.

At present no other mechanically polished metal surfaces are known to reproducibly yield such low values for surface roughness. Although roughness values approaching  $20 \text{ \AA rms}$  have been achieved in some laboratories, conventionally fabricated metal and alloys exhibit roughness in the 35 to  $50 \text{ \AA rms}$  range when mechanically polished.<sup>(1)</sup>

(1) H. E. Bennett, NWC, private communication.



## SUMMARY

### TECHNICAL PROBLEM

The objective of the program is to establish the material parameters necessary in each component of the mirror to obtain required performance. The goal is to achieve absorption  $\leq 0.1\%$  at  $\lambda = 10.6 \mu\text{m}$ . The validity of acquired information will then be demonstrated by producing a 4-component, 1.52-in.-diameter spherical mirror,  $R = 1.43 \text{ m}$ , exhibiting minimum reflectivity.

The specific objectives of Phase II were:

- 1) Prepare and evaluate high-conductivity, low-absorption sputter-deposited overlayers of pure copper and silver on flat polished ( $< 20 \text{ \AA}$  rms roughness) dispersion-hardened (1% SiC) copper substrates with the goal of demonstrating absorption of  $\leq 0.7\%$  for copper and  $\leq 0.5\%$  for silver.
- 2) Continue to develop the BNW India ink polishing process in order to demonstrate reproducible smooth surfaces. Improve the present grinding techniques so that surfaces optically flat to within one fringe can be reproducibly obtained.
- 3) Prepare dispersion-hardened (1 vol% SiC) deposits for polishing in optical facilities identified by NWC to obtain independent verification of polishability and to demonstrate control of optical figure.
- 4) Prepare dispersion-hardened (1 vol% SiC) copper deposits by high-rate sputtering onto mirror support materials of molybdenum, beryllium, copper, and alloy TZM<sup>R</sup>.
- 5) Initiate deposition and evaluation of selected materials for  $\lambda/4$  dielectric reflectivity enhancement coatings.
- 6) Initiate high-energy laser damage studies of the sputter-deposited high-conductivity copper and silver overlayers.

- 7) Reproduce the principal elements of the BNW differential calorimeter designed and constructed during Phase I for the purpose of establishing the same capability at NWC.

#### GENERAL METHODOLOGY

The chosen approach applies laboratory scale sputtering technology to the development of a mirror structure with subsequent characterization and evaluation of the structures formed.

#### TECHNICAL RESULTS

Polishability of sputter-deposited, dispersion-hardened copper was demonstrated in Phase I. Reproducibility was confirmed in Phase II by routine production of surfaces exhibiting roughnesses of  $\leq 20 \text{ \AA rms}$ . The material used, Cu-1 vol% SiC, was homogeneous with grain size of  $\leq 0.4 \text{ }\mu\text{m}$ . Deposits have been polished by three independent laboratories selected by NWC; all three achieved surface roughnesses below  $20 \text{ \AA rms}$ , and one repeatedly demonstrated surfaces with roughnesses of  $\sim 15 \text{ \AA rms}$ .

Thin ( $\approx 1500 \text{ \AA}$ ) sputtered, pure copper and silver overlayers were deposited on smooth ( $< 20 \text{ \AA rms}$ ) polished, dispersion-hardened copper substrates to reduce the infrared absorption in the surface. The minimum absorptions measured from these overlayers were 0.88% for copper and 0.83% for silver. Some deposition parameters important to minimizing absorption have been identified; they include:

- 1) Minimum sputter etching of the surface preceding deposition of the layer,
- 2) Deposition rate of  $\leq 250 \text{ \AA/min}$ ,
- 3) Substrate temperature of  $\approx 200^\circ\text{C}$ , and
- 4) Gas pressure and substrate spacing such that the deposition process is not diffusion controlled.

With further improvement, the goal of 0.7% absorption for copper and 0.5% for silver appears attainable.

The India ink polishing technique, developed during Phase I and documented in the Phase I report, did not yield reproducible results. During the present phase evidence has been obtained showing that free oxygen goes into solution when the ink slurry is exposed to air; this results in surface etching. Reducing the exposure of the ink to air has resulted in a 100% yield of polished samples.

Surfaces flat to within 1 fringe became mandatory to obtain reliable total reflectivity measurements on the reflectometer at NWC. Flat surfaces cannot be obtained using the present grinding techniques; the polishing pads used for grinding distort or flow irregularly resulting in nonreproducibility.

Candidate materials for deposition sources, substrates, and a suitable deposition system have been acquired for the deposition of the  $\lambda/4$  reflectivity enhancement coating (REC), but deposits have not been made.

The BNW developed TEA laser did not prove to be suitable for overlayer and REC laser damage studies. Therefore, two laboratories outside BNW were identified as having the required laser facilities and expertise to assist with the projected laser damage and subsequent analysis work.

Very preliminary damage data on samples produced under this program were obtained at Hughes Research Laboratory under the auspices of the Michelson Laboratory.<sup>(1)</sup> Polished 1% SiC-Cu exhibited a damage threshold of 130 joule/cm<sup>2</sup>; two sputtered Ag overlayers deposited on polished 1% SiC-Cu exhibited thresholds of 100 joule/cm<sup>2</sup> and 63 joule/cm<sup>2</sup>. Polished surfaces of OFHC-copper, Mo, and Be-Cu alloy tested under the same conditions exhibited damage thresholds of 34 joule/cm<sup>2</sup>, 43 joule/cm<sup>2</sup>, and 51 joule/cm<sup>2</sup>, respectively. Thus the sputtered materials exhibited damage thresholds a factor of 2 to 3 greater than bulk Be-Cu. Further, the sputtered Ag overlayers produced on this program did not reduce the damage threshold nearly as much as has been reported for silver deposited by vacuum evaporation.<sup>(2)</sup>

(1) M. J. Soileau, Private Communication, 1973.

(2) M. J. Soileau, Private Communication, 1973.

## DEPARTMENT OF DEFENSE IMPLICATIONS

The work in Phase I demonstrated that dispersion-hardened fine-grained metals can be mechanically polished to produce ultrasmooth surfaces. The work in Phase II indicates that sputter-deposited pure metal overlayers may be successfully employed for obtaining low IR absorption mirrors. This demonstration and the anticipated results in the third phase could greatly advance laser technology.

## IMPLICATIONS FOR FURTHER RESEARCH

Present results definitely establish the feasibility of producing a dispersion-hardened material by sputter deposition which can be mechanically polished to roughnesses below 20 Å rms. Further work is required to determine relationships between material properties and optical performance.

## SPUTTER DEPOSITION OF DISPERSION-HARDENED COPPER

Successful depositions on single mirror samples and subsequent polishing of dispersion-hardened material were obtained during Phase I. Since a large number of deposits were required for the study of the pure metal overlayer, the deposition system was redesigned and constructed to allow simultaneous deposition on four mirror substrates. A schematic presentation of the structure is given in Figure 1. The substrate holder and the target are water cooled. The basic system is a supported discharge (triode) system operating in the dc sputtering mode.<sup>(1,2)</sup> A concave substrate holder is used to achieve maximum uniformity of deposit thickness. The substrate is placed opposite the cathode at separations variable between 3.33 cm maximum and 2.22 cm minimum.

- (1) S. D. Dahlgren and E. D. McClanahan, "High Rate Sputtering of Stainless Steel," 3rd Symposium on Deposition of Thin Films by Sputtering, Rochester, N. Y., p. 20, 1969.
- (2) G. K. Wehner, Proceedings of Fifth International Conference on Ionization Phenomena in Gases, Munich 1961, North Holland Pub. Co., Amsterdam, Netherlands.

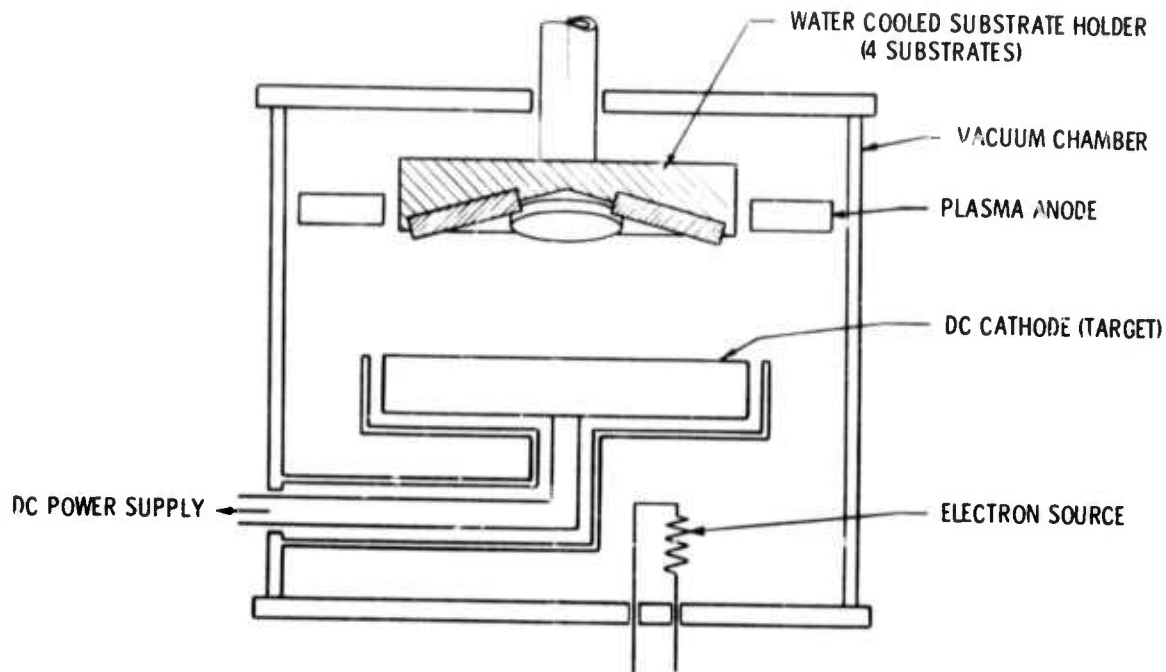


FIGURE 1. Schematic of Deposition System with Four Mirrors

The results obtained during Phase I led to the selection of the composition and deposition parameters deemed most favorable for the production of high-quality surface finishes. These conditions were:

Composition . . . . .	Copper - 1 vol% silicon carbide
Deposition Rate . . . . .	0.8 $\mu\text{m}/\text{min}$ <sup>(1)</sup>
Substrate Temperature . . . . .	$\leq 50^\circ\text{C}$
Substrate Bias . . . . .	0 or -20 volts
Substrate Surface . . . . .	Metallographic polishing plus brief electropolishing.

During the early stages of Phase II a deposit delamination problem occurred which defied solution for more than 2 months. Attempts to correlate the occurrence of delamination with deposition parameters failed

(3) The value 2  $\mu\text{m}/\text{min}$  presented in the Phase I report, p. 36, is in error.

although it was demonstrated that the new jiggling and geometry were not responsible. Delaminated deposits occurred at a deposition rate of  $0.8 \mu\text{m}/\text{min}$ . This rate was chosen to give greater stability of grain structure and to decrease the defect density in the deposit.

Under this program, time and budget did not allow pursuit of the important questions generated by deposit delamination. Although acceptable deposits can be obtained, a need clearly exists for additional investigation to understand delamination.

Without any strong evidence, two major changes in the procedure were made. First, the deposition rate was increased to  $\approx 1.1 \mu\text{m}/\text{min}$  and second, a new substrate preparation procedure was instituted. Substrates are now prepared by:

- 1) Metallographically polishing and finishing with Linde A alumina on a silk-MET cloth on a syntron vibratory polisher.
- 2) Electropolishing for 5 to 10 sec in 50% phosphoric acid-50% ethylene glycol.
- 3) Rinse in distilled water.
- 4) Wash in liquid detergent with cotton swabs.
- 5) Rinse in distilled water.
- 6) Rinse in deionized distilled water.
- 7) Place in reagent grade methyl alcohol for 5 min in ultrasonic cleaner.
- 8) Rinse with fresh reagent grade methyl alcohol just prior to inserting in sputtering chamber.

Although no scientific solution to the delamination problem was found, the above changes allowed production of the requisite number of mirror samples for Phase II work; delamination occurred in only one subsequent deposit. The deposit thickness was increased to  $0.015 \text{ in.}$  to allow extra material for grinding since flatness was added as a requirement. The deposition conditions used for all successful deposits of dispersion-hardened layers are presented in Table 1.

TABLE 1. Deposition Parameters for Dispersion-Hardened Copper Layers

Target . . . . .	Copper - 1 vol% SiC
Target-Substrate Spacing . .	22 mm
Sputtering Gas . . . . .	Krypton, research grade
Gas Pressure . . . . .	$2.5 \times 10^{-3}$ Torr
Substrate Etch . . . . .	5 min at -100 volts, 400 mA
Target Voltage . . . . .	-2000 volts
Target Current . . . . .	600 mA
Target amp-hrs . . . . .	3.5
Substrate Temperature . . .	$\leq 50^{\circ}\text{C}$ (water cooled copper holder)
Substrate Potential . . . .	-15 to -21 volts
Plasma Voltage . . . . .	35 volts
Plasma Current . . . . .	50 to 54 amp
Deposition Rate . . . . .	$\approx 1.1 \mu\text{m/min}$
Sputtering Yield . . . . .	13.4 to 13.9 g/amp hr
Deposit Thickness . . . . .	13.4 to 14.9 mils
Deposit Weight (each) . . .	3.4 to 4.2 g

#### SPUTTER DEPOSITION OF HIGH-CONDUCTIVITY OVERLAYERS

The principal goals of Phase II were to determine if sputter-deposited overlayers of a high-conductivity metal would exhibit absorption below that of the dispersion-hardened deposits and to obtain an absorption of 0.7% for copper overlayers. The initial experiments were performed using a high-purity copper target (MRC-MARZ Grade) depositing onto polished ( $<20 \text{ \AA}$  rms) dispersion-hardened copper substrates. Since more information exists regarding vacuum-deposited silver films, and since silver should exhibit lower IR absorption, the emphasis was changed to silver at the request of NWC. The balance of the work was, therefore, conducted with pure silver targets (MRC-MARZ Grade) to obtain a more meaningful comparison.

The initial intent was to investigate both rf and dc sputtered deposits and to evaluate their optical and, to the extent possible, their



electrical characteristics. Due to difficulties occurring with the dispersion-hardened deposits and the polishing procedure, only rf deposited layers have been investigated. The rf depositions were made in a simple rf diode sputtering system, schematically represented in Figure 2.

The electrode relationship with the substrate facing down is preferred since turbulence during initial pumpdown would otherwise increase the likelihood of small loose particles falling on the surface. The mirror sample is clamped with uniform pressure around the circumference to a temperature-controlled copper block. The high-purity metal target (Cu or Ag source) is placed on top of, rather than bonded to, the rf electrode, thus, avoiding contamination of the source due to bonding. The sputtering gas is reagent grade argon; the pressure in the system is controlled with a Granville-Phillips pressure controller combined with a Schultz-Phelps ionization vacuum gauge. A controlled constant gas flow is maintained in the system, regulated by the controller-operated needle inlet valve and a pump throttling valve. The pump throttling valve is a plate valve at the baseplate pumpout post. The orifice in the plate can be selected to obtain desired gas flow conditions; the valve can be removed during initial pump-down or whenever maximum conductance is required.

A brief discussion of the deposition parameters investigated and their expected influence on deposit properties follows.

#### SUBSTRATE ETCH

The polished mirror substrates were etched by ion bombardment preceding deposition of the overlayer. A plasma was generated in the system by applying an rf potential to the target. The shutter was located so that the plasma could reach the substrate while simultaneously preventing the deposition of sputtered material. Ion etching was accomplished by applying a selected dc potential to the substrate, negative with respect to the plasma potential. Etching cleaned the substrate. Absorbed gases and contaminant films were removed as well as a minimal number of surface atoms of the substrate material. Since excessive etching was expected

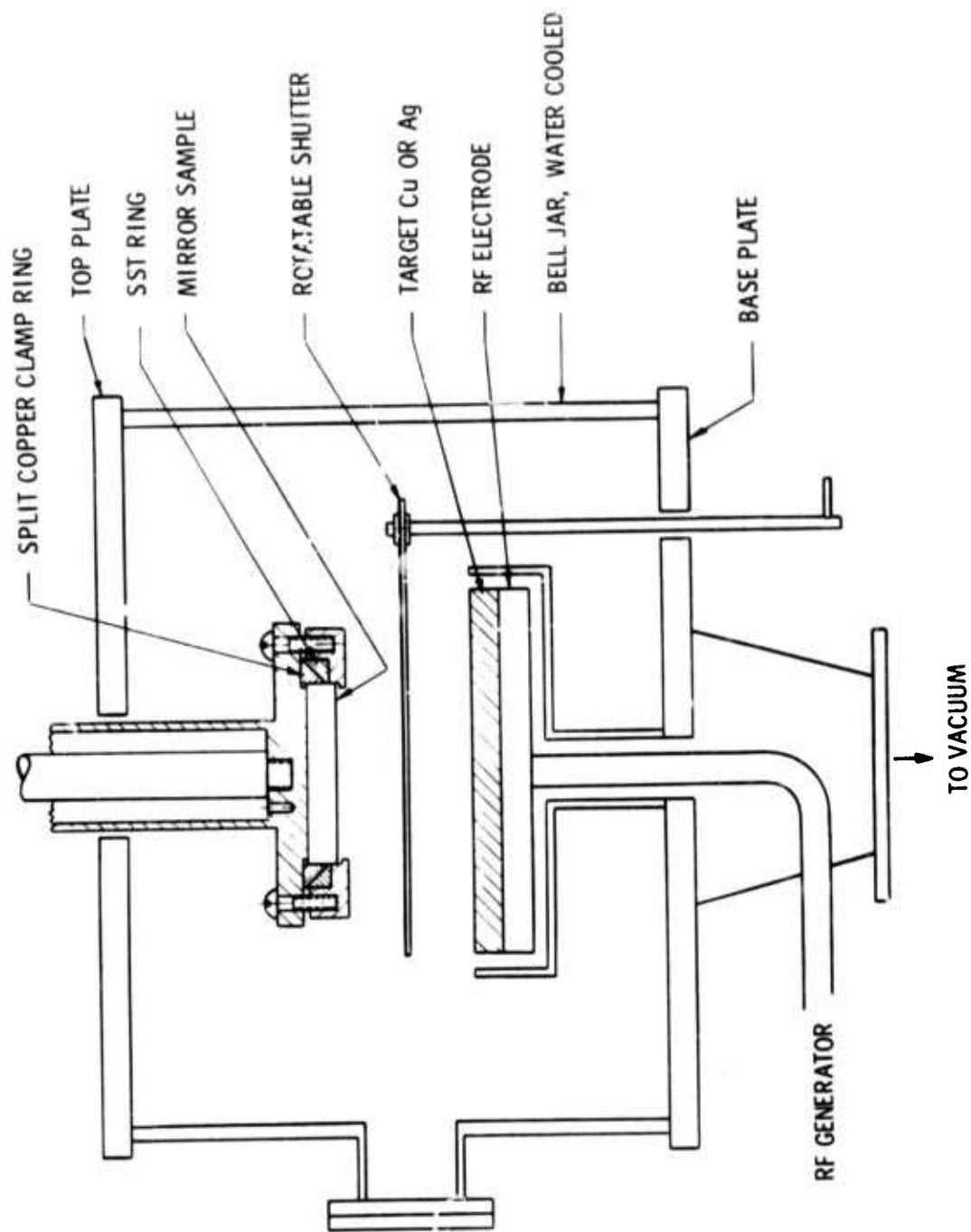


FIGURE 2. RF Sputtering Arrangement for High-Conductivity Metal Overlayers

to roughen the surface, four etch durations were employed to establish the extent of ion cleaning that could be used without affecting the surface quality.

#### SUBSTRATE TEMPERATURE

The temperature of the substrate, in addition to the sputtering gas pressure and deposition rate, determines the mobility of the adatoms arriving from the target. Thus a high temperature is expected to produce coarser grained structure and lower intrinsic stress levels than a lower temperature. The substrate temperature also influences dwell time or sticking probability of some impurity species arriving at the substrate. A low temperature therefore would be expected to contribute to more inclusions of certain impurities in the deposit. Substrate temperatures from 10°C to 250°C were therefore investigated.

#### DEPOSITION RATE

The deposition rate, expressed in units of thickness deposited per unit of time, affects the deposit purity as well as the deposit structure. High deposition rates effectively reduce adatom mobility and produce effects similar to a low substrate temperature since the time for trapping a mobile surface atom decreases with increasing deposition rate. Concentration of trapped impurities is determined by the arrival rate of the background (including sputtering gas) impurity atoms and respective dwell time at the surface and the arrival rate of deposited material. The deposition rate was varied from 250 to 1500 Å min.

#### TARGET-SUBSTRATE SPACING

The significance of this parameter lies not in its absolute value, but in the relation of the separation,  $L$ , to the mean-free path,  $\Lambda$ , of the sputtered atoms. If  $L/\Lambda < 1$ , the sputtered atoms, on the average, do not collide with atoms of the sputtering atmosphere and arrive at the substrate with their original momentum and energy. This condition leads to

"line of sight" deposition. If  $L/\lambda > 1$ , the sputtered atoms are randomized, deposition becomes diffusion controlled, and atoms arrive at the substrate with reduced energies. Target-to-substrate separation was varied from 2.54 cm to 6.35 cm. In the pressure range from 5 to 10 millitorr used in these depositions, 1-in. separation corresponds to  $\frac{L}{\lambda} \approx 1$  while 6.35-cm separation corresponds to  $\frac{L}{\lambda} > 1$  for both copper and silver.

#### PREPARATION OF LOW ROUGHNESS DISPERSION-HARDENED COPPER MIRROR SUBSTRATES

Late in Phase I and early in Phase II, surfaces with roughnesses  $< 20 \text{ \AA}$  rms could not be reproducibly obtained. The difficulty was initially attributed to a change in the manufacturing procedure employed by the supplier of the polishing pads.<sup>(1)</sup> Using the initially successful pads did not resolve the problem. The procedure was therefore re-examined.

Discrepancies were observed between calorimetric absorption measurements at BNW and absolute reflectivity measurements at NWC. It was demonstrated that the discrepancy was due to a lack of flatness in BNW-polished samples. One of the 1 vol% SiC-Cu samples exhibited a reflectivity of 0.980 at  $\lambda = 10.6 \text{ \mu m}$  in the NWC reflectometer. Upon rotating the sample  $90^\circ$  the observed reflectivity changed to 0.983. Although this amounts to only a 0.3% difference in observed reflectance, the change in implied absorption,  $\alpha = 1-R$ , is 15%. The discrepancy lies far outside the accuracy of both the absolute reflectometer at the Michelson Laboratory and the calorimeter at BNW.

To obtain a valid comparison between the two instruments, considerable effort was expended in attempts to produce smooth surfaces exhibiting flatness to within one fringe. This effort continued until it was established that the grinding technique employed was not suitable for producing optical flats. The emphasis was then shifted to determine the applicability of sputtering as a method for depositing pure, high-conductivity metal overlayers on smooth dispersion-hardened copper substrates. Descriptions of the grinding and polishing efforts follow.

(1) Geoscience Instrument Corp., Mount Vernon, New York.

## SAMPLE POLISHING

The basic India ink polishing procedure used was developed during Phase I and documented in the Phase I report. The technique employs a bowl-feed apparatus with a lap of Politex-D polishing cloth and a slurry based on India ink. The important parameters include the pH of the polishing slurry, duration of polishing, and the pressure applied to the sample during polishing. Smooth surfaces ( $<20 \text{ \AA rms}$ ) were not reproducibly obtained and it was observed that an apparent unpredictable etch effect was present. Therefore electrode potential measurements between Cu and Pt immersed in the ink were measured. In all cases, copper was negative with respect to platinum, indicating that positive ions were leaving the copper electrode. In one test, the copper electrode potential,  $\phi_{\text{Cu}}$ , changed from  $\phi_{\text{Cu}} = -0.13$  volts to  $\phi_{\text{Cu}} = -0.27$  volts after 15 minutes exposure to air. In another test, addition of 37 ml of a concentrated solution of the reducing agent, hydroquinone, to 1200 ml of ink solution caused  $\phi_{\text{Cu}}$  to change from  $\phi_{\text{Cu}} = -0.11$  volts to  $\phi_{\text{Cu}} = -8.4 \times 10^{-3}$  volts in 19 minutes.

The tests support the following model for the etching process: ink exposed to air free oxygen goes into solution. The free oxygen acts as an oxidizing agent, releasing cupric ion into solution. It is well known<sup>(1)</sup> that cupric ion ( $\text{Cu}^{++}$ ) forms a complex with ammonia,  $\text{Cu}^{++} + 4\text{NH}_3 \rightarrow \text{Cu}(\text{NH}_3)_4^{++}$ . Since ammonium hydroxide is the agent added to the ink to keep carbon black particles in suspension, a plentiful supply of  $\text{NH}_3$  is present in the ink. Thus, oxidation of the copper and subsequent complexing by dissolved  $\text{NH}_3$  produces etching of the copper. It can also be noted that a weak solution of  $\text{NH}_4\text{OH}$  in  $\text{H}_2\text{O}_2$  is used as a light etch in preparing copper samples for metallography.<sup>(2)</sup> These results were taken as evidence that the problem was partly due to excessive oxygen concentration in the ink.

The presence of an etch effect in the ink was clearly demonstrated when a 30-min, 1/4-micron diamond grind was included as a final step before

(1) G. B. King and W. E. Caldwell, The Fundamentals of College Chemistry, Amer. Book Co., New York, N. Y., 1951, p. 409.

(2) G. L. Kehl, The Principles of Metallographic Laboratory Practices, McGraw-Hill, New York, N. Y., 1949, p. 419.

polishing to further improve the final mirror surface finish. It was observed, however, that surfaces thus produced were etched more readily in the ink solution. The Nomarski photographs in Figure 3 show a comparison between a 1/4-micron and a 1-micron final grind. In contrast to the finely cut surface appearance resulting from a 1-micron grind, the surfaces produced by the 1/4-micron grind had a burnished appearance, possibly indicating that the surface contained much more stored energy. This apparently highly worked surface was attacked more severely by the etching of the ink.

The removal of the 1/4-micron diamond final grind coupled with the use of freshly prepared ink which minimized the exposure of the ink slurry to air resulted in reproducibly and routinely produced surfaces with roughnesses of less than  $20 \text{ \AA rms}$ . The pH was 9, the polishing time 9 min., and the sample pressure  $90 \text{ g/cm}^2$ .

#### FLAT SAMPLE GRINDING

Reliable measurements at NWC of total reflectivity can apparently be made only on flat samples. Since the India ink polish only requires 9 min., the change in mirror figure due to polishing can be neglected and the figure must, therefore, be achieved during the grinding stages.

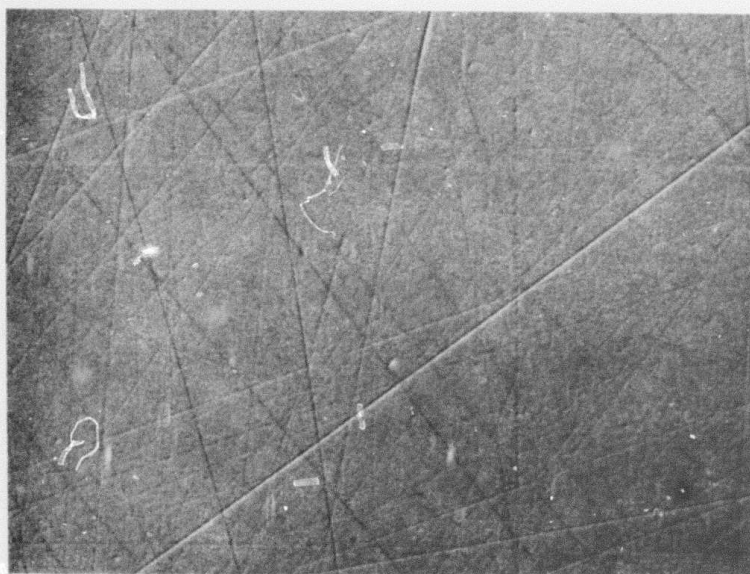
The sputtered dispersion-hardened Cu deposits were ground in seven stages before the final polishing step. Monotonically decreasing diamond grit size was used in the successive steps. Grinding at each stage continued until marks from the previous stage could not be seen at 40X magnification. The grit sizes, approximate grinding time for each step, and the lap used are presented in Table 2.

This procedure resulted in surfaces with flatnesses about 2 fringes in mercury light. It was found that the polishing pads would flow and distort much more severely than the pitch lap. Distortions were produced in the pad and only by carefully positioning the sample to follow such distortions could the desired flatness be achieved. One flat sample, within 1 fringe, was obtained using this method but the procedure was not





(a)



(b)

320X

**FIGURE 3.** Nomarski Photos. (a) 1/4- $\mu$  Grind on 1% SiC-Cu Sample  
(b) 1- $\mu$  Grind on 1% SiC-Cu Sample.



TABLE 2. Grinding and Polishing Schedule

Stage	Diamond Grit Size, Microns	Approximate Time, Min	Lap Material
1	30	10	Mylar
2	15	10	Mylar
3	15	15	Black Politex-D <sup>(1)</sup>
4	9	15	Black Politex-D
5	6	20	Black Politex-D
6	3	30	Black Politex-D
7	1	60	Black Politex-D

(1) Geoscience Instruments Corporation, Mount Vernon, N. Y.

reproducible. Acceptable flat samples for calorimetric measurements, about 2 fringes, were obtained by grinding single samples and by carefully ensuring that the part was moving over the entire surface of the pad during grinding.

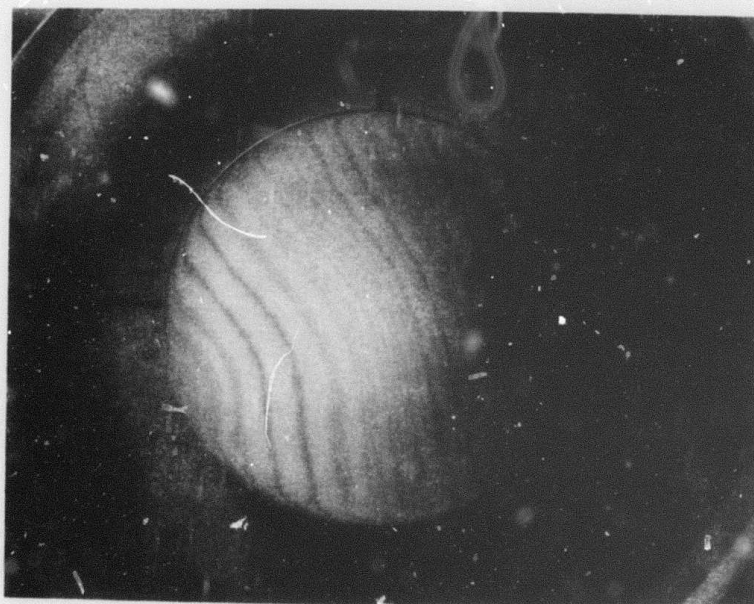
Figure 4 shows a simple flatness test in mercury light on Sample 010. Figure 4(a) was made at the 1-micron grind stage and Figure 4(b) after polishing and silver deposition. These represent typical results obtained from a number of samples.

Initially distortion of the mirror figure was introduced by the mount used during deposition of the metal overlayer. A new mount was designed and constructed in which uniform clamping pressure over the circumference of the mirror sample was achieved which eliminated all measurable distortion caused by the mounting technique.

Inability to obtain surface flatness is not associated with the material or the polishing techniques. It is a problem associated with the grinding procedure used for which no acceptable solution has been found. Sputtered, dispersion-hardened samples have been successfully polished to flat figure by other optical houses. Their grinding procedures are scheduled to be transmitted to BNW from NWC.



(a)



(b)

FIGURE 4. Interference Fringes in Hg Light Between Optical Flat, Sample 010. (a) 1- $\mu$  Grind (b) After India Ink Polish and Ag Deposition

## SURFACE EVALUATION

### SCATTERED LIGHT MEASUREMENTS

An instrument for relative measurement of surface roughness based on scattered light from the surface was designed, constructed and used in Phase I. A detailed description with typical data is given in the Phase I report.

Briefly the intensity of H<sub>g</sub>-Ne light scattered at an angle  $\theta$  by the test sample is compared to that scattered at  $\theta$  by a metallized standard quartz sample provided by NWC. The standard has a surface roughness of 10.83 Å rms. Forward scattering measurements are made for  $20^\circ < \theta < 75^\circ$  from the surface normal at  $5^\circ$  intervals. The angle of incidence is  $5^\circ$ . Representative data obtained from sample 043-27, using this procedure, is presented in Figure 5. Routine measurements such as these are obtained by using an  $8^\circ$  angle of acceptance to the photo multiplier tube, which is used as the detector in the scattering instrument. A more detailed analysis of the surface was obtained by substituting a smaller aperture ( $1.71^\circ$ ) in the PM tube and by making measurements every  $2^\circ$  instead of every  $5^\circ$ . These measurements are presented in Figure 6. In both figures, the ordinate represents the ratio of light scattered by the test sample to that scattered by the standard sample at the same scattering angle.

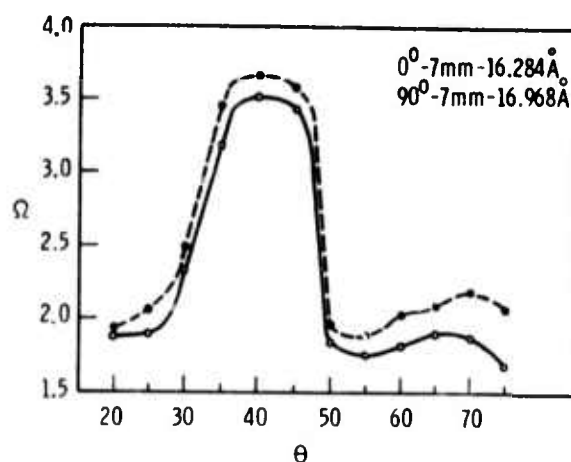


FIGURE 5. Scattering Data for Sample 043-27;  
 $8^\circ$  Acceptance Angle, Data Every  $5^\circ$

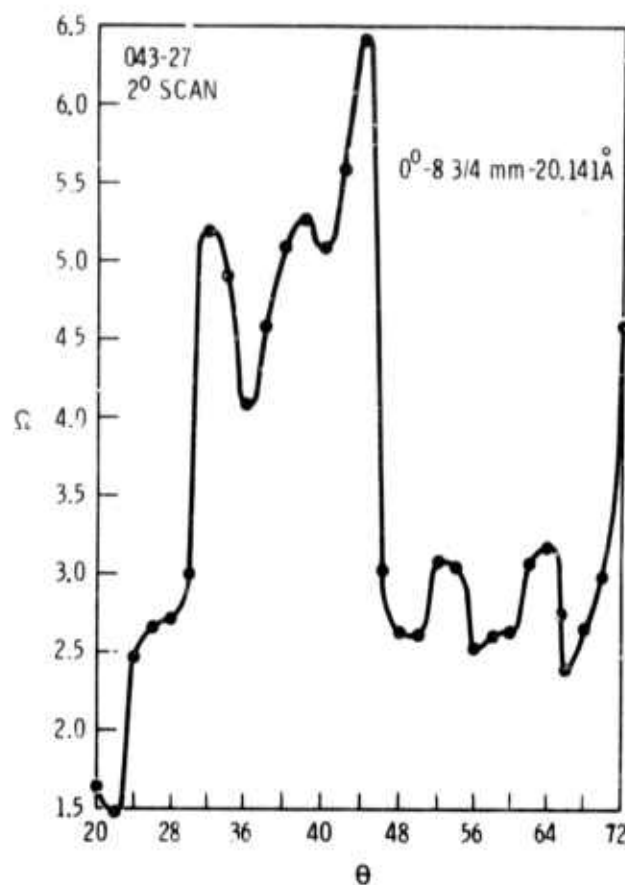


FIGURE 6. Scattering Data for Sample 043-27;  
1.7° Acceptance Angle, Data Every 2°

Structure apparent in the fine scan can be interpreted as arising from a basic periodicity in the surface of the sample; see Figure 6. The theory of scattering from a periodic surface<sup>(1)</sup> shows that light is scattered into preferred directions specified by the grating equation,

$$\sin \theta_{2m} = \sin \theta_1 + m\lambda/\Lambda \quad (1)$$

where  $m = 0, \pm 1, \pm 2, \dots$

$\theta_1$  = angle of incidence

$\lambda$  = wavelength of light = 6328 Å

and  $\Lambda$  = spatial wavelength of surface periodicity.

(1) P. Beckmann and A. Spizzichano, The Scattering of Electromagnetic Waves from Rough Surfaces, Pergamon Press, New York, N. Y., 1963, p. 34 et seq.

Angular positions of maxima in Figure 6 correspond to orders  $m = -5, -6, \dots -12$  for  $\Lambda = 8.7 \pm 0.25 \mu\text{m}$ .

Although structure in the scattered field is evident in Figure 5, the large aperture used in obtaining that data acts to integrate over an  $8^\circ$  segment of the field and to eliminate the lobes observed in Figure 6. Thus, analysis of Figure 5, assuming that it represents details of the scattered field distribution, would lead to incorrect results for periodicity of the surface. Such analyses were previously reported in Appendix A of the Phase I report but they are believed to be erroneous in the light of present results.

Three samples were analyzed with this technique and the results are shown in Table 3. The balance of the samples were given the routine analysis established in Phase I. Origin of the periodicity observed is not definitely known but it is most likely due to the presence of residual grinding marks which were not removed in the finer grinding stages.

TABLE 3. Summary of Periodicity Analyses

<u>Sample</u>	<u>m</u>	<u><math>\Lambda</math>, micron</u>
041-19	-9... -16	12.0
043-27	-5... -12	8.7
007	-5... -10	10.4

#### ABSORPTION MEASUREMENTS

A twin-type calorimeter was designed, constructed, and calibrated during Phase I; the details are presented in Phase I report. The calorimeter has since been used for routine absorption measurements at  $10.6 \mu\text{m}$  for all observations of absorption in sputter-deposited metal overlayers produced in Phase II.

Under normal procedure, the mirror is mounted in the test cell of the calorimeter and the system is allowed to reach thermal equilibrium. A Coherent Radiation Labs (CRL) Model 42  $\text{CO}_2$  laser is then turned on and allowed to stabilize with the output beam intercepted by an electrically

controlled shutter. The shutter is then opened and the laser beam illuminates the central portion of the test mirror. Reflected energy is measured by a CRL Model 201 power meter positioned at 3°47' from the mirror normal. By adjusting the exposure time and laser output power, each measurement is made to correspond to approximately 3 joules of absorbed energy in the sample mirror.

Data is reduced by planimeter integration of the chart records of both the time versus temperature history of the calorimeter and of the reflected power versus time curve observed on the power meter. The calorimeter calibration constant was determined to be  $0.4799 \pm 0.01$  joules/in.<sup>2</sup> of the calorimeter chart. The calibration of the power meter chart was checked on each exposure. For  $E_a$  ( $E_r$ ) as the absorbed (reflected) energy, the absorption  $\alpha$  is given by

$$\alpha = \frac{E_a}{E_a + E_r} \quad .$$

The reflectivity is then given by  $R = 1 - \alpha$ . Consistent good agreement between BNW absorption measurements and NWC total reflectivity measurements has not been obtained, possibly due to lack of flatness of the sample mirror, as previously discussed.

## RESULTS

The deposition parameters were studied in groups of experiments within which only one parameter was varied. All the sample surfaces were examined by Nomarski microscopy and scattered light before and after application of metal overlayers. Calorimetric absorption measurements were performed on the metal overlayer only. A summary of the results for copper and silver overlayers are presented in Tables 4 and 5, respectively.

It can be seen from the data presented in Tables 4 and 5 that the combined effects of sputter etching and deposition contribute to a slight increase in surface roughness. Excluding samples E-4 and E-12, to be



**TABLE 4. Copper Depositions**

### Group I. Effect of Substrate Etching

Constants: Etch conditions . . . . . 100 volts, 1.0 to 1.6 mA  
Substrate temperature . . . . . 100 to 127°C  
Deposition rate . . . . . 500 Å/min  
Target-substrate separation . 2 1/2 in.

Deposition	Etch Time (min)	Surface Roughness ( $\text{\AA}$ )		Absorption (%)
		Substrate	Overlayer	
B-1	0	12	20	1.26
B-2	2	17	20	1.02
B-3	5	21	22	1.00
B-4	31	12	19	1.07

### Group II. Effect of Deposition Rate

Constants: Substrate etch. . . . . 20 min at -100 volts  
 $\approx 1$  mA  
 Substrate temperature . . . . 100 to 116°C  
 Target-substrate separation . 2 1/2 in.

Deposition	Deposition Rate (Å/min)	Surface Roughness (Å)		Absorption (%)
		Substrate	Overlayer	
C-1	500	14	19	0.95
C-2	250	15	19	0.88
C-3	1000	16	19	0.95

TABLE 5. Silver Depositions

### Group I. Effect of Substrate Etching

Constants: Etch conditions. . . . . 100 volts  
Substrate temperature. . . . . 100°C  
Target-substrate spacing. . . . . 2 1/2 in.

Deposition	Deposition	Etch Time (min)	Surface Roughness (Å)		Absorption (%)
	Rate (Å/min)		Substrate	Overlayer	
D-2	500	20	17	24	2.06
E-2	500	5	20	19	1.76
D-3	1500	20	15	19	2.07
E-1	1500	5	16	19	2.03



TABLE 5. (contd)

## Group II. Effect of Substrate Temperature

Constants: Etch . . . . . 5 min 100 volts 0.5 mA  
 Deposition rate . . . . . 250 Å/min  
 Target-substrate spacing . 2 1/2 in.

Deposition	Substrate Temp. (°C)	Surface Roughness (Å)		Absorption (%)
		Substrate	Overlayer	
E-5	10	17	21	1.29
E-6	100	16	18	1.13
E-10	175	14	18	0.89
E-4	250	15	>50	0.83

## Group III. Effect of Deposition Rate

Constants: Etch . . . . . 5 min 100 volt 0.5 mA  
 Substrate Temperature . . 100°C  
 Target-substrate spacing . 2 1/2 in.

Deposition	Deposition Rate (Å/min)	Surface Roughness (Å)		Absorption (%)
		Substrate	Overlayer	
E-1	1500	16	19	2.03
E-2	500	20	19	1.76
E-6	250	16	18	1.13

## Group IV. Effect of Target-Substrate Spacing

Constants: Etch. . . . . None  
 Deposition rate . . . . . 250 Å/min  
 Substrate Temperature . . 100°C

Deposition	Spacing (in.)	Surface Roughness (Å)		Absorption (%)
		Substrate	Overlayer	
E-7	2 1/2	14	75	1.01
E-8	1 3/4	17	20	0.95
E-3	i	17	19	0.86
E-9	1	13	13	0.90

discussed below, the average change in roughness due to both etching and deposition was  $+3.5 \text{ \AA}$ , while five samples experienced roughness changes less than  $1.5 \text{ \AA}$ . It can be concluded that conditions can be defined for which roughness change upon deposition will be less than  $1.5 \text{ \AA}$ .

Silver overlayers D-1 and E-4 both had a "milky" appearance. Nomarski Photos of these surfaces are shown in Figures 7 and 8. Deposition conditions for these samples were at the two extremes of substrate temperature; D-1 was deposited at  $10^\circ\text{C}$  at a rate of  $500 \text{ \AA/min}$ , while E-4 was deposited at  $250^\circ\text{C}$  at  $250 \text{ \AA/min}$ . Both overlayers were subjected to a polish in India ink for 4 minutes with light weight; both were made smoother. In sample D-1, the absorption decreased from  $\alpha = 0.0216$  to  $\alpha = 0.0176$  with a roughness change from  $23.6 \text{ \AA}$  to  $16.5 \text{ \AA}$ . Sample E-4 originally had a roughness greater than  $50 \text{ \AA rms}$ . Polishing in ink reduced that value to  $16.2 \text{ \AA}$ , but with this sample the absorption increased from  $\alpha = 0.0083$  to  $\alpha = 0.0105$ . Subsequent annealing of sample E-4 for 1 hour at  $200^\circ\text{C}$  in vacuum increased the roughness to  $20 \text{ \AA rms}$  but the absorption decreased to  $\alpha = 0.0092$ .

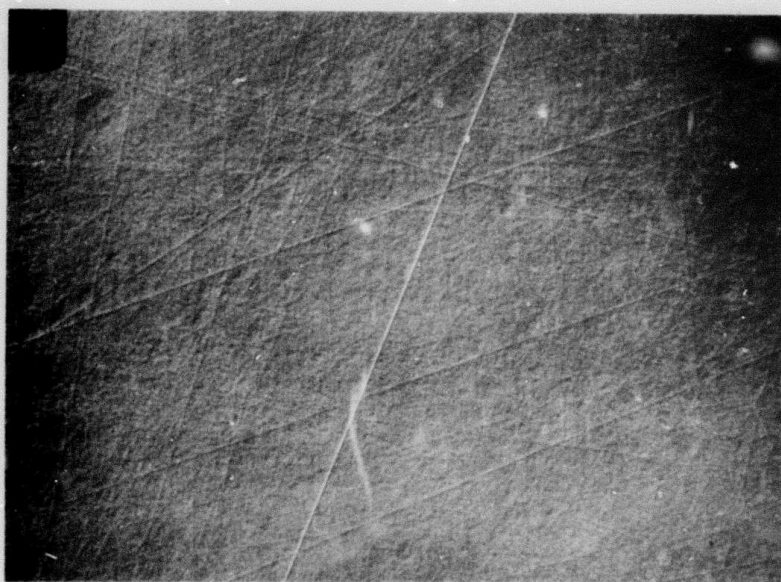
These results demonstrate that the ink process can be used to polish extremely thin ( $\approx 1500 \text{ \AA}$ ) layers of silver with minimal deleterious effects. Since sample D-1 was deposited at  $10^\circ\text{C}$  and sample E-4 at  $250^\circ\text{C}$ , the absorption results are not surprising. In the as-deposited condition, sample E-4 was probably in a much lower energy state because of the higher substrate temperature. Polishing sample E-4 may have caused work hardening of the surface which was relieved to some extent by subsequent annealing. Polishing of sample D-1 in ink definitely reduced roughness and probably acted to release energy stored in the film. Many more experiments will be necessary to establish definite cause and effect relationships. Experiments reported here serve to identify fruitful areas for further research.

Absorption measurements at  $10.6 \text{ \mu m}$  can be analyzed using results of the modified Drude theory.<sup>(1)</sup> According to that theory the reflectance

(1) H. E. Bennett and J. M. Bennett, "Validity of the Drude Theory for Silver, Gold, and Aluminum in the Infrared," Optical Properties and Electronic Structure of Metals and Alloys, North Holland Pub. Co., Amsterdam, p. 175, 1966.



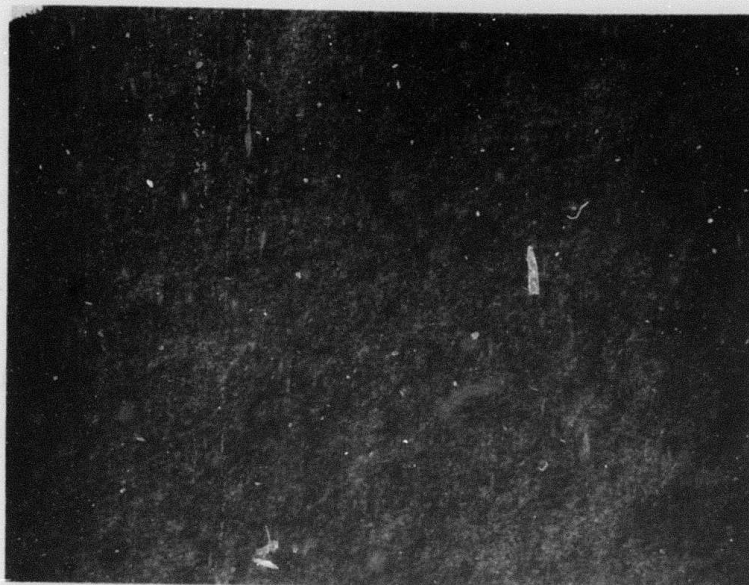
(a)



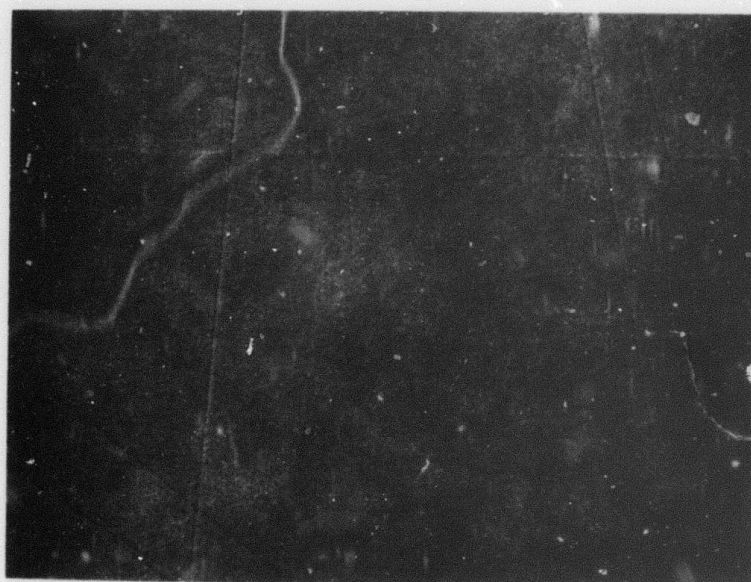
(b)

FIGURE 7. Nomarski Photos for Ag Overlayer D-1.  
 (a) As Sputtered, Surface Roughness 23.6 Å  
 (b) After 4 Minutes of India Ink Polish,  
 Surface Roughness 16.5 Å





(a)



(b)

FIGURE 8. Nomarski Photos for Ag Overlayer E-4.  
(a) As Sputtered, Surface Roughness  $>50 \text{ \AA}$   
(b) After 4 Minutes of India Ink Polish,  
Surface Roughness  $16 \text{ \AA}$

R is given by

$$R = \exp\left\{-\frac{2\omega}{\pi\sigma_0} [(\omega^2\tau^2 + 1)^{1/2} - \omega\tau]\right\} . \quad (2)$$

In Equation (2),  $\omega$  represents the angular frequency of the light,  $\sigma_0$  the dc electrical conductivity, and the  $\tau$  the electron relaxation or mean time between collisions for electrons. Since the reflectance is related to mirror absorption,  $\alpha$ , by

$$R = 1 - \alpha , \quad (3)$$

Equation (2) can be solved for  $\sigma_0$  in terms of absorption:

$$\sigma_0 = \frac{2\omega}{\pi} \frac{[(\omega^2\tau^2 + 1)^{1/2} - \omega\tau]}{[\ln(1-\alpha)]^2} . \quad (4)$$

Simple transport theory gives the conductivity as

$$\sigma_0 = \frac{ne^2\tau}{m} \quad (5)$$

where  $n$  represents number density,  $e$  electronic charge, and  $m$  electron effective mass. Consequently, the absorption data can be used either to calculate a conductivity assuming a relaxation time or by combining Equation (4) and Equation (5) to calculate a relaxation time assuming a value for  $n$ , the number density of electrons. Presence of any imperfection or impurity in the sputtered overlayer will act to decrease the relaxation time, making choice of any published value of relaxation time at best questionable. In our experience, the densities normally attained by the sputtering process lie between 90% and 100% of theoretical. Consequently, the approach expected to provide some insight into the electrical properties of the overlayers is to solve Equation (4) and (5) for the relaxation time in terms of absorption at  $10.6 \mu\text{m}$ . The result is:

$$T = \frac{1}{A(\alpha) \sqrt{1 + 2 \frac{\omega}{A(\alpha)}}} \quad (6)$$

$$\text{where } A(\alpha) = \frac{[\ln(1-\alpha)]^2 \pi n e^2}{2\omega m} \quad (7)$$

In the absence of any film density measurements, we will assume  $n$  to be 95% of the bulk value for both Cu and Ag. The bulk value for copper is  $n_{\text{Cu}} = 8.5 \times 10^{22} \text{ cm}^{-3}$  and for silver is  $n_{\text{Ag}} = 5.85 \times 10^{22} \text{ cm}^{-3}$ . Bulk values for relaxation times are  $T_{\text{Cu}} = 2.45 \times 10^{-14} \text{ sec}$  and  $T_{\text{Ag}} = 3.82 \times 10^{-14} \text{ sec}$ .

For copper the inferred relaxation times lie between 39% and 57% of the bulk value. The silver results are lower and cover the range of 16% to 47% of bulk value. No consistent reason for the difference between copper and silver results can be seen at this time. Data at present is insufficient to test the anomalous skin effect.

Minimum absorption observed in copper overlayers is 0.88% and in silver is 0.83%. The lowest reported values for absorption at  $10.6 \mu\text{m}$  are 0.7% for copper and  $\approx 0.4\%$  for silver. The data indicates that the favored deposition conditions are:

- 1) Minimum etching,<sup>(1)</sup>
- 2) Low deposition rate,
- 3) As high a substrate temperature as is consistent with retaining a low-roughness surface, and
- 4) Close spacing of target and substrate.<sup>(1)</sup>

Deposition E-10 was an attempt to optimize each of the above parameters. Although the resulting absorption was nearly as low as that achieved in earlier experiments, the high absolute value ( $\alpha = 0.89\%$ ) prompted the investigation of additional variables. The low values obtained for relaxation

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(1) When the spacing is less than about 1 1/2 inches, it becomes difficult to etch the substrate with the shutter in place since the plasma tends to be excluded from the necessarily narrow gap between the substrate and shutter.

times and the polishing results with D-1 and E-4 indicated that the overlayers contained a high-impurity level. An investigation of the purity of the sputtering atmosphere was therefore conducted.

In the first experiment (E-11), the gas flow rate was reduced to about one-tenth of that normally used. The deposition conditions were the same as for deposition E-7 and the absorption was significantly higher (1.17 versus 1.01%). This indicated that the walls of the sputtering chamber were acting as a significant source of impurity gases. It was therefore decided to thoroughly clean the chamber and its internal fixtures and to bake the assembly to the temperature limits imposed by the polymeric vacuum seals before the next run.

In run E-12, the plasma was ignited and maintained at 500 watts for 1 hour with the substrate protected by the shutter. Unfortunately, the effect of the system cleanup by baking and plasma operation was obscured by impurities released from the hot shutter which condensed on the relatively cooler substrate. The deposit surface roughness was 32 Å rms and the absorption was 1.64%. The experiment was to be repeated with a cooled shutter but work on the program was stopped before this deposition was performed. In separate work, however, it was learned that even with a clean baked system, the initiation of the plasma produced a broad spectrum of impurities including chlorine and hydrocarbons. The partial pressures of these species diminished very slowly, e.g., after 1 hour they were still about 10% of their original values. Since the overlayer depositions were made with a "presputtering" period (plasma on, shutter in place) of about 10 minutes, except as noted above, the atmosphere was probably poor in all cases.

When work is resumed, a deposition under optimum parameter values will be made, using a residual gas analyzer to indicate when the atmosphere is sufficiently clean to begin depositing. To use the small spacing and shield the substrate from sputtered atoms, it will be necessary to have the shutter very close to the substrate. Substrate etching will then have to be performed with the shutter in the withdrawn position. Although it is possible to apply a sufficiently high bias voltage to the



substrate during etching to assure a negative net deposition rate, cone formation may occur on the substrate surface due to the presence of two species of different sputtering yields.<sup>(1-4)</sup> If this occurs to an extent which causes observable roughening of the surface, it will be necessary to modify the apparatus to permit the target-substrate spacing to be changed while under vacuum.

### CONCLUSIONS

- 1) The concept, first demonstrated in Phase I, of sputter depositing dispersion-hardened copper to form a metallic surface polishable to a roughness less than 20 Å rms has been confirmed. Once the polishing procedure was re-established, all of the nonlaminated samples deposited during Phase II were polished to this quality.
  - 2) Grinding using polishing cloth cannot reproducibly produce optical flats.
  - 3) The infrared absorption is minimized in thin copper and silver overlayers as a function of the following four primary parameters:
    - a) Minimum etching of the substrate surface,
    - b) Low deposition rate (250 Å/min),
    - c) Moderate-to-high substrate temperature ( $\approx 200$  C), and
    - d) Small separation of target and substrate ( $\approx 1$  in.).
  - 4) Purity of sputtering atmosphere, an additional parameter, emerged as a significant variable. Although the deleterious effects of an impure atmosphere are and were well known, it was not realized until late in Phase II that the atmosphere in the sputtering chamber was as impure as indicated above. This is believed to be responsible for the higher than anticipated absolute absorption values.
- 
- (1) S. D. Dahlgren and E. D. McClanahan, J. Appl. Phys., vol. 43, pp. 1514-1517, 1972.
  - (2) G. K. Wehner and D. J. Hajicek, J. Appl. Phys., vol. 42, p. 1145, 1971.
  - (3) G. S. Anderson, J. Appl. Phys., vol. 40, p. 2884, 1969.
  - (4) G. S. Anderson, J. Appl. Phys., vol. 36, p. 1558, 1965.

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